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<p>(54) Title: INKS COMPOSITIONS AND THEIR USE IN INK JET PRINTING</p> <p>(57) Abstract</p> <p>A composition comprising a water-dissipatable polymer, dye, surfactant, water and organic solvent, wherein the surfactant comprises: (a) a surfactant having a sulpho or sulphate group; or (b) a non-ionic surfactant free from carbon-carbon triple bonds; or (c) a mixture of (a) and (b). The compositions are useful as an ink jet printing inks or as a concentrates from which such inks may be prepared. The compositions and inks have particularly good operability in ink jet printers and low viscosities may be achieved.</p>		

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INKS COMPOSITIONS AND THEIR USE IN INK JET PRINTING

This invention relates to compositions, to inks and to their use in ink jet printing.

Ink jet printing methods involve printing an image onto a substrate using ink droplets emitted from a small nozzle without bringing the nozzle into contact with the substrate. Over recent years ink jet printers have become popular because they are
5 quieter and more versatile than impact printers, for example conventional basket typewriters are noisy and the images they can print are restricted to the shapes moulded onto the end of each mechanical lever. The most popular ink jet printers are the thermal and piezoelectric.

10 WO 98/14524 of Zeneca describes ink compositions comprising water, a water-dissipatable polyester, a dye and various solvents.

Although the inks described in WO 98/14524 are stated as having good properties, there is a continual need to improve the performance of ink jet printing inks. In particular, low viscosities are desirable because thermal ink jet printers can have difficulties in firing high viscosity inks. The quality of printed text is also of commercial
15 importance in terms of edge sharpness, optical density, light fastness, mottle and ink penetration. If inks penetrate too much then undesirable "strike through" occurs where the printed image is visible on the reverse side of printed paper. Ink jet printing inks are also required to have good storage stability and operability, i.e. low tendency to block the tiny nozzles used in ink jet print heads.

20 We have now found that certain surfactants can improve the properties of compositions such as those described in WO 98/14524 and other polymer-containing ink jet printing inks.

According to the present invention there is provided a composition comprising a water-dissipatable polymer, dye, surfactant, water and organic solvent, wherein the
25 surfactant comprises :

- (a) a surfactant having a sulpho or sulphate group; or
- (b) a non-ionic surfactant free from carbon-carbon triple bonds; or
- (c) a mixture of (a) and (b).

30 The water-dissipatable polymer preferably bears non-ionic and/or ionic water dispersing groups, preferably ionised carboxy and/or sulphonate groups, especially ionised sulphonate groups, because these assist water dissipatability of the polymer. Such groups can be chain pendant and/or terminal.

The water-dissipatable polymer is preferably a water-dissipatable acrylic,
35 polyurethane or polyester, more preferably a water-dissipatable polyester.

The water-dissipatable polyester can be prepared using conventional polymerisation procedures known to be effective for polyester synthesis. Thus, it is well

known that polyesters contain carbonyloxy (i.e. -C(=O)-O-) linking groups and may be prepared by a condensation polymerisation process in which an acid component (including ester-forming derivatives thereof) is reacted with a hydroxyl component. The acid component may be selected from one or more polybasic carboxylic acids, e.g. di-
5 and tri-carboxylic acids or ester-forming derivatives thereof, for example acid halides, anhydrides or esters. The hydroxyl component may be one or more polyhydric alcohols or phenols (polyols), for example, diols, triols, etc. (It is to be understood, however, that the polyester may contain, if desired, a proportion of carbonylamino linking groups - C(=O)-NH- (i.e. amide linking groups) by including an appropriate amino functional
10 reactant as part of the "hydroxyl component"; such as amide linkages). The reaction to form a polyester may be conducted in one or more stages. It is also possible to introduce in-chain unsaturation into the polyester by, for example, employing as part of the acid component an olefinically unsaturated dicarboxylic acid or anhydride.

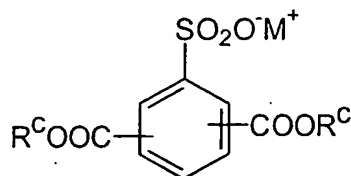
Polyesters bearing ionised sulphonate groups may be prepared by using at least
15 one monomer having two or more functional groups which will readily undergo an ester condensation reaction (e.g. carboxyl groups, hydroxyl groups or esterifiable derivatives thereof) and one or more sulphonic acid groups (for subsequent neutralisation after polyester formation) or ionised sulphonate groups (i.e. neutralisation of the sulphonic acid groups already having been effected in the monomer) in the synthesis of the polyester. In
20 some cases it is not necessary to neutralise sulphonic acid groups since they may be sufficiently strong acid groups as to be considerably ionised in water even without the addition of base. Often, the sulphonic acid or ionised sulphonate containing monomer is a dicarboxylic acid monomer having at least one ionised sulphonate substituent (thereby avoiding any need to effect neutralisation subsequent to polyester formation).
25 (Alternatively, alkyl carboxylic acid ester groups may be used in place of the carboxylic acid groups as ester-forming groups). Such a monomer will therefore be part of the acid component used in the polyester synthesis.

Preferred polybasic carboxylic acids which can be used to form the polyester have two or three carboxylic acid groups. For example, one can use C_4 to C_{20} aliphatic,
30 alicyclic and aromatic compounds having two or more carboxy groups and their ester forming derivatives (e.g. esters, anhydrides and acid chlorides), and dimer acids such as C36 dimer acids. Specific examples include adipic acid, fumaric acid, maleic acid, succinic acid, itaconic acid, sebacic acid, nonanedioic acid, decanedioic acid, 1,4-cyclohexanedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, 1,2-
35 cyclohexanedicarboxylic acid, terephthalic acid, isophthalic acid, phthalic acid and tetrahydrophthalic acid and their acid chlorides. Anhydrides include succinic, maleic, phthalic and hexahydrophthalic anhydrides.

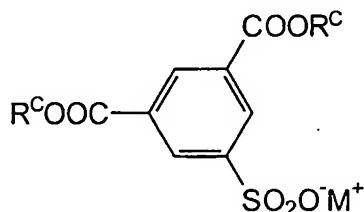
Preferred polyols which can be used to form the polyester include those having from 2 to 6, more preferably 2 to 4 and especially 2 hydroxyl groups per molecule.
40 Suitable polyols having two hydroxy groups per molecule include diols such as 1,2-

ethanediol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, 2,2-dimethyl-1,3-propanediol (neopentyl glycol), the 1,2-, 1,3- and 1,4-cyclohexanediols and the corresponding cyclohexane dimethanols, diethylene glycol, dipropylene glycol, and diols such as alkoxyated bisphenol A products, e.g. ethoxylated or propoxylated bisphenol A. Suitable polyols having three hydroxy groups per molecule include triols such as trimethylolpropane (1,1,1-tris (hydroxymethyl)ethane). Suitable polyols having four or more hydroxy groups per molecule include pentaerythritol (2,2-bis(hydroxymethyl)-1,3-propanediol) and sorbitol (1,2,3,4,5,6-hexahydroxyhexane).

Compounds having two or more groups which readily undergo an ester condensation reaction and have one or more sulphonate groups are dicarboxylic acid monomers having at least one ionised sulphonate group. Examples of such compounds are aromatic dicarboxylic acids having an ionised sulphonate group, for example those of the formula:

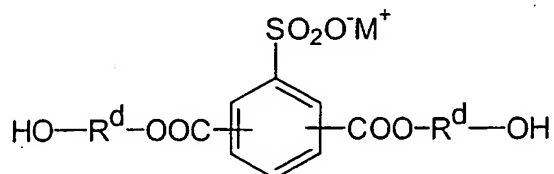


wherein M is a cation (preferably sodium, lithium or potassium); and each R^c independently is H, a cation or C₁₋₄-alkyl (preferably methyl or ethyl). Preferred compounds of the above formula are of formula:



wherein M and R^c are as defined above. Particularly preferred is the mono sodium salt, this material being known as sodio-5-sulphoisophthalic acid (SSIPa).

Other useful compounds which have two or more groups which readily undergo an ester condensation reaction and have one or more sulphonate groups are dihydroxy monomers having at least one sulphonate group, especially those of the formula:



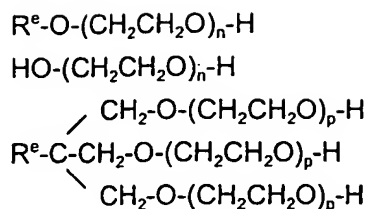
wherein M is as hereinbefore defined above and each R^d independently is alkylene, preferably C₂₋₄-alkylene. Preferred compounds of the above formula are:



wherein M is as hereinbefore defined.

Polyesters bearing ionised carboxy groups can be prepared by various means. For example, if the hydroxyl component of the reactants is stoichiometrically in excess of the acid component, a hydroxyl-terminated polyester can be formed, which may be subsequently converted to a carboxy terminated polyester by wholly or partially reacting the hydroxyl groups with an appropriate reagent (e.g. an acid anhydride or a dicarboxylic acid). Alternatively, terminal carboxy functionality may be directly introduced by employing an appropriate stoichiometric excess of the acid component reactants. In another alternative, chain-pendant carboxy groups may be introduced by using reagents such as dimethylol propionic acid (DMPA) since if appropriate reaction condition are employed (e.g. polymerisation temperature below 150°C) the hindered carboxy group thereof does not take part to any significant extent in the ester-forming reactions during the polyester synthesis and the DMPA effectively behaves as a simple diol. Chain-pendant and/or terminal carboxy groups could also be introduced by employing a tri- or higher functionality carboxylic acid or anhydride in the polyester synthesis, for example, trimellitic acid or anhydride. Combinations of the above procedures could also be used. It is thus seen that terminal or side-chain carboxy groups or both can be introduced as desired. These can be fully or partially neutralised with an appropriate base to yield ionised carboxy groups. The counter ions used may be as for the ionised sulphonate groups described above (apart from H⁺ since the carboxylic acid groups themselves are normally insufficiently ionised to provide a significant amount of ionised carboxy groups - although F substituents would increase acid strength), with alkali metal ions such as Na⁺, Li⁺ and K⁺ again being particularly preferred, and ammonium and organic amine derived cations less preferred because some have an undesirable odour.

The water-dissipatable polyester may optionally have hydrophilic non-ionic segments, for example within the polyester backbone (i.e. in-chain incorporation) or as chain-pendant or terminal groups. Such groups may act to contribute to the dispersion stability or even water-solubility of the polyester. For example, polyethylene oxide chains may be introduced into the polyester during its synthesis by using as part of the hydroxyl component, ethylene oxide-containing mono, di or higher functional hydroxy compounds, especially polyethylene glycols and alkyl ethers of polyethylene glycols, examples of which include:



5

wherein R^e is C_{1-20} -alkyl, preferably C_{1-4} -alkyl, more preferably methyl; n is 1 to 500; and p is 1 to 100.

10 A small segment of a polyethylene oxide chain could be replaced by a propylene oxide or butylene oxide chain in such non-ionic groups, but should still contain ethylene oxide as a major part of the chain.

The amount of ionised sulphonate and/or carboxy groups present in the polyester should be sufficient to provide or contribute to water-dissipatability of the polyester, although it should not be so high as to render the resulting polyester unacceptably water-sensitive. This amount will depend, inter alia, on factors such as the hydrophilicity/ hydrophobicity of units provided by other monomers in the polyester synthesis or any surfactants (if used), and also the relative proportions of ionised sulphonate/carboxy groups. With regard to the last mentioned point, ionised sulphonate groups are more effective at providing or contributing to water-dissipatability than ionised carboxy groups and so can be used at considerably lower levels in comparison to ionised carboxy groups.

15 If the polyester is wholly or predominantly sulphonate stabilised (by which is meant the water dissipatability-providing groups are provided wholly or predominately by ionised sulphonate groups). The ionised sulphonate group content is preferably within the range from 7.5 to 100 milliequivalents (more preferably 10 to 75 milliequivalents and particularly 11 to 56 milliequivalents) per 100 g of polyester. When using SSIPA as the monomer for providing the ionised sulphonate groups, the amount of this monomer used in the polyester synthesis, based on the weight of all the monomers used in the polyester synthesis, will usually be within the range from 2 to 20% by weight (more usually 3 to 15% by weight). The carboxylic acid value (AV) of the polyester which is predominantly sulphonate stabilised, i.e. an AV based on the carboxylic acid groups only (i.e. excluding sulphonate groups) will generally be within the range of from 0 to 100 mgKOH/g, more preferably 0 to 50 mgKOH/g, especially 0 to 25 mgKOH/g, more especially 0 to 10mgKOH/g.

20 If the polyester is predominantly stabilised by ionised carboxy groups, the carboxylic acid value AV of the polyester is preferably within the range of from 20 to 140 mgKOH/g (more preferably 30 to 100 mgKOH/g).

Usually, the polyester is either predominantly sulphonate-stabilised or predominantly carboxylate stabilised (preferably the former).

40 If the polyester contains polyethylene oxide chains, the polyethylene oxide chain content should preferably not exceed 25% by weight (and more preferably should not

exceed 15% by weight), based on the total weight of the polyester, in order to avoid unacceptable water-sensitivity. Therefore the amount is preferably 0 to 25% by weight (more preferably 0 to 15% by weight) based on the total weight of polyester.

5 The water-dissipatable polyester preferably has a number average molecular weight M_n of up to 30,000. The M_n is preferably in the range from 1000 to 30,000, more preferably 1500 to 25,000, especially 2000 to 20,000. These M_n lead to particularly good storage stability for the resultant inks. The measurement of M_n is well known to those skilled in the art, and may for example be effected using gel permeation chromatography in conjunction with a standard polymer such as polystyrene or polymethylmethacrylate of
10 known molecular weight.

The water-dissipatable polyester preferably has a hydroxyl number of from 0 to 225mg KOH/g, more preferably 0 to 125mg KOH/g, especially from 0 to 50mgKOH/g.

The T_g of the water-dissipatable polyester (i.e. the temperature at which the polymer changes from a glassy, brittle state to a plastic, rubbery state) is preferably in the
15 range -38°C to 105°C , more preferably -20 to 70°C , especially -10°C to 60°C .

The esterification polymerisation processes for making the polyesters for use in invention composition are known and need not be described here in more detail. Suffice to say that they are normally carried out in the melt using catalysts, for example a tin-based catalyst, and with the provision for removing any water or alcohol formed from the
20 condensation reaction.

The water-dissipatable polyester may be dissipated in water by adding the solidified melt directly into water. The solidified melt is preferably in a form such as flake (which can often be obtained directly from the melt) or comminuted solid (obtained for example by grinding). Alternatively, water can be added directly to the hot polyester melt
25 until the desired solids content/viscosity is reached. Still further, the polyester may be dissipated in water by adding an aqueous pre-dissipation (or organic solvent solution) of the polyester to the water phase.

The water-dissipatable polyesters normally do not need an external surfactant when being dissipated into water, although such surfactants may be used to assist the
30 dissipation if desired and in some cases can be useful in this respect because additional surfactants reduce the required amount of dissipating groups (i.e. sulphonate, and (mono alkoxy)polyalkylene chains if used).

Water-dissipatable polyesters can also be purchased from Eastman Kodak Company and Avecia Limited. Examples include Eastman AQ29D and AQ55W.

35 The water-dissipatable polymer may also be formed by performing free radical polymerisation of olefinically unsaturated monomers in the presence of a polyester. This gives what could be called a polyester-acrylic hybrid. Olefinically unsaturated monomers which can be used include olefinically unsaturated carboxy functional monomers, e.g. acrylic acid, methacrylic acid, fumaric acid, itaconic acid and β -carboxyethyl acrylate;
40 olefinically unsaturated monomers which are free from carboxy and hydroxy groups, e.g.

1,3-butadiene, isoprene, styrene, vinylidene halides, vinylidene esters and esters of acrylic acid and methacrylic acid, e.g. methyl (meth) acrylate, ethyl (meth)acrylate n-butyl (meth)acrylate and 2-ethyl hexyl (meth)acrylate; and olefinically unsaturated monomers having a hydroxy group e.g. N-methylol (meth)acrylamide and hydroxy C₂₋₈-alkyl esters of (meth)acrylic acid. If the polyester has been prepared using a component which has unsaturation therein, e.g. fumaric acid, maleic acid or muconic acid or allyl-containing dihydroxy or dicarboxy compounds, the product from the polyesterification reaction will have unsaturation incorporated into its structure which can take part in the free radical polymerisation to give a graft copolymer. The free radical polymerisation processes use a free-radical generating initiator system such as (for example) the redox radical initiator system tertiary butylhydroxide/isoascorbic acid and will take place in the aqueous phase, rather than in the melt. However, excessive amounts of acrylic polymer (whether formed in the presence of polyester which has unsaturation or is free from unsaturation) often leads to a deterioration in ink properties and it is preferred that no acrylic polymer is present or, if its is present, the amount is less than 40%, preferably less than 30%, more preferably less than 10% by weight relative to the weight of polyester.

Preferably the aqueous medium is water or a mixture of water and one or more organic solvent, more preferably a mixture comprising water, one or more water-immiscible organic solvent and one or more water-miscible organic solvent.

Preferred water-dissipatable acrylic polymers are as described in International patent application No. PCT/GB99/00705, page 1, line 23 to page 6, line 17 which is incorporated herein by reference thereto. Preferred water-dissipatable polyurethane polymers are as described in International patent application No. PCT/GB99/00655, page 1, line 22 to page 4, line 39 which is incorporated herein by reference thereto.

Preferred dyes are essentially insoluble in water and are preferably soluble in organic solvents. Disperse and solvent soluble dyes are preferred, especially those carrying a branched alkylamino group because this results in compositions having particularly good light fastness.

Disperse and solvent soluble dyes are distinct from pigments in that pigments are insoluble in organic solvents whereas disperse and solvent soluble dyes are soluble in organic solvents. Useful classes of disperse and solvent soluble dyes include water-insoluble anthraquinones, phthalocyanines, pyrrolines, triphenodioxazines, methines, benzodifuranones, coumarins, indoanilines, benzenoids, xanthenes, phenazines, solvent soluble sulphur dyes, quinophthalones, pyridones, aminopyrazoles, pyrrolidines, styrylics and azoics. Examples of preferred azoics are monoazo, disazo and trisazo disperse dyes and solvent soluble dyes; especially preferred azoics contain heterocyclic groups. The Colour Index International lists suitable disperse and solvent soluble dyes, examples of which include Solvent Blue 63, Disperse Blue 24, Solvent Black 3, Solvent Black 35 and Disperse Red 60.

Further examples of disperse dyes are given in the Colour Index, 3rd Edition, Volume 2, pages 2483 to 2741 and further examples of solvent soluble dyes are given in Volume 3, pages 3566 to 3647 and each of these dyes is included herein in reference.

The dyes are preferably in a purified form, preferably over 90%, more preferably over 95%, especially over 98% pure.

Surfactants carrying sulpho ($-\text{SO}_3^-$) groups include alkyl benzene sulphonic acid salts (e.g. ArylanTM surfactants from Akcros); aromatic sulphonic acid salts (e.g. EltesolTM surfactants from Albright & Wilson); and preferably mono- and di- alkyl (especially mono- and di- C_4 to C_{18} -alkyl) sulposuccinates and mono- and di-alkyl sulposuccinamates (e.g. EmpiminTM surfactants from Albright & Wilson), mono- and di-alkyl (especially mono- and di- C_4 to C_8 -alkyl), ethoxy succinates (e.g. EmpiminTM surfactants from Albright and Wilson). Especially preferred anionic surfactants are di-isooctyl sulposuccinates, especially the sodium, potassium, lithium and ammonium and substituted ammonium salts thereof.

Surfactants carrying sulphate groups ($-\text{SO}_4^{2-}$) include alcohol sulphates and ether sulphates, preferably hydroxy C_{6-18} -alkyl sulphates and $\text{C}_{6-18}\text{-O}(\text{CH}_2\text{CH}_2\text{O})_x \text{SO}_3\text{H}$ wherein X is from 1 to 10 inclusive. Such surfactants are available under the Empicol trade mark from Albright & Wilson.

The preferred non-ionic surfactants include fatty alcohol alkoxyates (e.g. Synperonic A or 91 from ICI); fatty acid alkoxyates (e.g. EMPILAN BQTM surfactants from Albright & Wilson); alkyl and aryl phenol alkoxyates (e.g. EMPILAN NPTM surfactants from Albright & Wilson); also fatty acid esters of polyethylene glycols e.g. (Ethylan A series from Ackros); castor oil ethoxyates (e.g. DEHSCOFIX COTM surfactants from Albright & Wilson); sorbitan esters and their ethoxyates (e.g. SPANTM and TWEENTM surfactants from Aldrich); and ethylene oxide-propylene oxide block copolymers (e.g. SYNPERONIC PETM surfactants from ICITM), in each case being free from carbon - carbon triple bonds.

Preferably the surfactant has a number average molecular weight below 1000.

The compositions preferably exist as a solution, emulsion, micro-emulsion, dispersion or micelle. Preferably the compositions are inks, especially inks suitable for use in a thermal and/or piezoelectric ink jet printers.

Preferably the compositions contain less than 500ppm, more preferably less than especially 100ppm, especially less than 50ppm, more especially less than 20ppm in total of divalent, trivalent metal cations, metal cations and halide anions. "ppm" means parts per million by weight relative to the weight of the composition. Compositions of this purity may be prepared by purifying an impure composition, or the components which go into the composition, using standard purification techniques. Suitable techniques include reverse osmosis, ultrafiltration, ion exchange and combinations thereof.

For best results the compositions are prepared by mixing (i) a solution of the dye in water, an organic solvent or a mixture of water and an organic solvent; with (ii) a mixture of the water-dissipatable polymer and water, optionally containing an organic

solvent; wherein said surfactant is present in (i) or (ii) or (i) and (ii). Addition of said surfactant after the dye solution and water-dissipatable polymer solution have been mixed works less well.

5 Preferably the compositions have a viscosity of less than 8, more preferably less than 6, especially less than 3 centipoise at 20°C. Preferably the compositions have a surface tension less than 50mN/m, more preferably less than 40mN/m, at 20°C.

The amount of each component in the composition will vary according to the depth of shade required and the properties desired. Typically, however, the composition will comprise :

- 10 (i) from 30 to 95 parts, more preferably from 40 to 80 parts of water;
- (ii) from 1 to 70 parts, more preferably from 5 to 60 parts, especially from 10 to 30 parts of organic solvent;
- (iii) from 0.1 to 20 parts, more preferably from 0.5 to 10 parts, especially from 0.5 to 5 parts of dye;
- 15 (iv) from 0.25 to 40 parts, more preferably from 0.5 to 20 parts, especially from 1 to 8 parts of water-dissipatable polymer; and
- (v) from 0.10 to 15 parts, more preferably from 0.25 to 10 parts, especially from 0.5 to 7 parts of surfactant;

wherein said surfactant comprises;

- 20 (a) an anionic surfactant;
- (b) a non-ionic surfactant free from carbon-carbon triple bonds; or
- (c) a mixture comprising (a) and (b); and

wherein all parts are by weight and the number of parts (i)+(ii)+(iii)+(iv)+(v) add up to 100.

25 The number of parts of the water-dissipatable polymer is calculated on a 100% solids basis. For example 50g of a 20% solids polymer is taken as 10g (or 10 parts) of polymer.

The organic solvent (as mentioned in (ii) above) preferably comprises a water-miscible organic solvent and a water-immiscible organic solvent because this leads to particularly good dye solubility and ink stability.

30 Suitable water-immiscible organic solvents are as described in WO 98/14524, page 11, lines 16 to 30, which are incorporated herein by references thereto, and optionally substituted nicotinamides e.g. nicotinamide-N-oxide and nicotinamide; optionally substituted furfuryl alcohol e.g. 2,5-furandimethanol and furfuryl alcohol; optionally substituted tetrahydrofurfuryl alcohol, e.g. 5-methyl tetrahydrofuran-2-methanol, methyl tetrahydrofurfuryl ether and tetrahydrofurfuryl alcohol; alkyl and aryl lactates e.g. butyl lactate and benzyl lactate; and mixtures of any two or more of the foregoing. Benzyl alcohol is especially preferred.

Suitable water-miscible organic solvents are as described in WO 98/14524, page 11, line 31 to page 12, line 7, which is incorporated herein by reference thereto.

The water-immiscible solvent preferably has a solubility in water at 20°C of up to 50g/l. The water-miscible solvent preferably has a solubility in water at 20°C of more than 50g/l.

5 The ratio of water-miscible organic solvent to water-immiscible organic solvent is preferably 20:1 to 1:2, more preferably 19:1 to 1:1, especially 8:1 to 1:1, more especially 5:1 to 1:1.

10 The compositions may be prepared by mixing the components thereof in any order. Conveniently the water-dissipatable polymer is coloured with the dye and the resultant coloured water-dissipatable polymer is then mixed with the remaining components of the composition. Suitable methods for coloring the water-dissipatable polymer are described in WO 98/14524, page 10, line 16 to page 11, line 12, which is incorporated herein by reference thereto.

15 The compositions of the invention are particularly useful as ink jet printing inks, demonstrating a low tendency for blocking the nozzles of thermal ink jet printers, low viscosities (valuable for thermal ink jet printers), good quality of prints and good storage stability.

20 The presence of the particular surfactants stated in claims, especially those having a sulpho or sulphate group, allow lower loading of the water-dissipatable polymer to be achieved and gives more stable inks. These inks have a low tendency for phase separation or crystal formation and a low tendency to block nozzles in the ink jet printers. The di-isooctyl sulphosuccinates are particularly beneficial in this regard.

According to a second feature the present invention there is provided a process for printing an image on a substrate comprising applying thereto a composition according to the first aspect of the invention by means of an ink jet printer.

25 The ink jet printer emits droplets of the ink onto a substrate from a nozzle without bringing the nozzle into contact with the substrate. Preferably the ink jet printer is a thermal or piezoelectric ink jet printer. Normally the ink jet printer will be fitted with a printer head which is not adversely affected by the contents of the ink, e.g. it may be coated or otherwise treated to withstand the solvents contained in the ink.

30 The substrate is preferably a paper, an overhead projector slide or a textile material. Preferred textile materials are cotton, polyester and blends thereof.

Preferred papers are plain or treated papers and films which may have an acid, alkaline or neutral character. Examples of commercially available treated papers include HP Premium Coated Paper (available from Hewlett Packard Inc), HP Photopaper
35 (available from Hewlett Packard Inc), Stylus Pro 720 dpi Coated Paper, Epson Photo Quality Glossy Film (available from Seiko Epson Corp.), Epson Photo Quality Glossy Paper (available from Seiko Epson Corp.), Canon HR 101 High Resolution Paper (available from Canon), Canon GP 201 Glossy Paper (available from Canon), and Canon HG 101 High Gloss Film (available from Canon).

When the substrate is a textile material the process for printing an image thereon according to the invention preferably further comprises the step of heating the resultant printed textile, preferably to a temperature of 50°C to 250°C.

5 The inks of the present invention may also be used for the preparation of colour filters, for example those used in flat bed displays.

A third aspect of the present invention provides a paper, an overhead projector slide or a textile material printed with a composition according to the second aspect of the present invention or by means of a process according to the second aspect of the present invention.

10 A fourth aspect of the present invention provides an ink jet printer cartridge containing a composition according to the first aspect of the present invention.

The invention is further illustrated by the following examples in which all parts and percentages are by weight unless specified otherwise. In these Examples the following abbreviations are used :

15 Paper XA is Xerox 4024 from Rank Xerox.

Paper GB is Gilbert Bond paper from the Mead Corporation.

Paper WC is Wiggins Conqueror High White Wove 100g/m² from Arjo Wiggins Ltd.

" - " means not measured.

20 Solperse™ 27000 is a non-ionic surfactant free from carbon-carbon triple bonds from Avecia Limited, England.

Synperonic™ PE L72, PE L35 and PE 85 are ethylene oxide/propylene oxide block copolymer surfactants from ICI Ltd.

25 Empimin™ MH and MKB are mono alkyl sulphosuccinamate surfactants from Albright & Wilson.

Tween™ 80 is an ethoxylated sorbitan ester surfactant from Aldrich.

Surfynol™ 465 is a non-ionic surfactant containing carbon-carbon triple bonds from Air Products (See comparative example).

30

Preparation of Water-Dissipatable Polymers

Resin X

A water-dissipatable polymer was prepared as described for Resin 3 in WO 98/145254, (page 21 from "water-dissipatable polymer ("Resin 3")" to end of page 21).

35 This polymer is referred to as "Resin X" in the following Examples.

Resin V - A sulpho acrylic resin (20/90/50)

Component	Name	Parts
1	2-pyrrolidone	100
2	butyl acrylate	13.5
3	sodium styrene sulphonate	3
4	styrene	13.5
5	3-mercaptopropionic acid	0.9
6	Initiator V65	0.99144
7	2-pyrrolidone	16
8	Initiator V65	0.24786
9	2-pyrrolidone	4

Components 1 to 5 were placed in a reaction flask purged with nitrogen. The components were stirred under nitrogen until all reagents were dissolved. The reaction flask was heated to, and then held at 65°C, a solution of 6 in 7 was added and the reaction continued with agitation for 4 hours. After 4 hours a solution of 8 in 9 was added and the reaction allowed to continue for a further 1 hour before being cooled and filtered. The resultant water-dissipatable polymer had a solids content of 20%, a Mn of 2279 and a Mw of 3326.

Resin W - A sulpho acrylic resin

Component	Name	Parts (weight)
1	2-pyrrolidone	100
2	butyl acrylate	13.5
3	sodium styrene sulphonate	3
4	methylmethacrylate	13.5
5	3-mercaptopropionic acid	0.9
6	Initiator V65	3.368
7	2-pyrrolidone	16
8	Initiator V65	0.842
9	2-pyrrolidone	4

Components 1 to 5 were placed in a reaction flask purged with nitrogen. The components were stirred under nitrogen until a homogenous solution had formed. The mixture was then heated to 60°C and a solution of 6 in 7 was added. The mixture was kept at 65°C with agitation for 4 hours, after which a solution of 8 in 9 was added. The mixture was agitated at 65°C for a further 1 hour before cooling and stored in a bottle.

The resultant water-dissipatable acrylic polymer had a solids content of 20%, a Mn of 3460 and a Mw of 6319.

Resin Y - An acrylic resin (20/90/57)

Component	Name	Parts (weight)
1	methylethylketone	100
2	butyl acrylate	10.5
3	methacrylic acid	3
4	polyethylene glycol methacrylate mol wt 1000	3
5	hydroxyethylmethacrylate	3
6	methylmethacrylate	10.5
7	3-mercaptopropionic acid	0.9
8	Initiator V65	0.984
9	methylethylketone	16
10	Initiator V65	0.246
11	methylethylketone	4

5 Components 1 to 7 were placed in a reaction flask purged with nitrogen. The contents were stirred under nitrogen until a homogenous solution had formed. The mixture was then heated to 65°C, a solution of 8 in 9 was added. The mixture was agitated at 65°C for 4 hours, after which a solution of 10 in 11 was added. The reaction was allowed to continue for a further 1 hour before cooling and bottling. The resultant water-dissipatable acrylic polymer had a solid content of 20%, a Mn of 4264 and a Mw of 8157.

10

Resin Z - A 50:50 mixture of acrylic and polyurethane resins

Resin Z is a 50:50 mixture by weight of an acrylic polymer (Polymer A) and a polyurethane polymer mixture (polymer P) and was prepared as follows:

Step (i) Preparation of Polymer A (MAA/MMA/BA = 10/69.5/20.5)

Component	Materials	Weight (g)
a	<u>De-ionised Water</u>	436.5
b	<u>Monomer Feed</u> Methacrylic acid Methyl methacrylate Butyl acrylate 3 Mercaptopropionic acid	37.35 259.68 76.47 11.07
c	<u>Initiator Feed</u> Ammonium persulphate De-ionised water Sodium lauryl sulphate	3.73 120.5 5.60
d	<u>Burn-up Co-initiator</u> Ascorbic acid De-ionised water	2.243 42.58
e	<u>Burn-up Initiator</u> t-Butyl hydrogen peroxide (70% solids) De-ionised water	3.20 41.62
f	<u>Odour reducer</u> Hydrogen peroxide solution (30% solids)	2.49
g	De-ionised water to take to 30% solids	250
h	<u>Neutralisation</u> Ammonia solution 20%	36.91

10% of b (omitting the methacrylic acid) was added to the reaction and stirred for 5 minutes. 20% of c was added and the mixture stirred for 15 minutes to seed the reaction.

The remainder of b and c were added over 90 minutes, maintaining the temperature of the mixture at 80-83°C. The mixture was maintained at 80-83°C for a further hour before cooling to 50°C.

Component d was added drop-wise over 30 minutes, during which time e was added in three equal shots at 1, 10 and 20 minutes. The mixture was stirred for a further 30 minutes, then f was added drop-wise over 10 minutes. g was added, followed by h to give a clear latex which was cooled and filtered to remove particulate matter.

The resultant Polymer A has a pH of 7.19, solids content of 29.73%, Mn of 5811 and Mw of 13837.

Step (ii) Preparation of Polymer P

5

Materials	Weight (g)
<u>Pre-polymer</u>	
Dimethylol propionic acid (DMPA)	3.0
1,4 Cyclohexanedimethanol (CHDM)	8.25
Polypropylene glycol 1000 (PPG1000)	27.91
Isophorone diisocyanate (IPDI)	35.84
Dibutyl tin dilaurate (DBTDL)	0.08
N-methyl -2- pyrrolidinone (NMP)	18.75
<u>Termination</u>	
Jeffamine M1000	115.26
<u>Dispersion</u>	
Ammonia (35% solution)	1.38
De-ionised water	545.67

DMPA, CHDM, PPG1000 and NMP were added to a reaction flask and stirred under N₂.

10 IPDI was added and the mixture was heated to 50°C with continuous stirring under nitrogen gas. DBTDL was added and the mixture heated to 90°C and held there for 3 hours. The NCO content was measured periodically and when it reached 4.81% the Jeffamine M1000 was added and the mixture stirred for a further hour at 90°C.

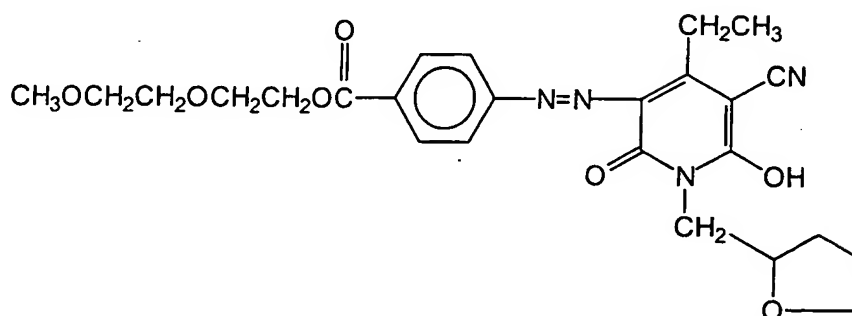
15 The mixture was dispersed in the mixture of ammonia and water with continuous stirring, followed by a further hour stirred without applying heat. Particulate matter was removed by filtering the dispersion through a cloth having a pore size of 50µm, to give a first polyurethane polymer having a pH of 9.4, Mn 4343, Mw 6676, surface tension of 37.68mN/m and viscosity @ 10% solids of 2.47cps.

20 The first polyurethane (10g) was diluted with de-ionised water (15g) and mixed thoroughly with a dispersion of NeoRez R-985 (18.75g, a commercially available polyurethane dispersion from Avecia) in de-ionised water (56.25g).

The resultant mixture is polymer P.

Step (iii) Preparation of Resin Z

Equal weights of the products of step (i) and step (ii) were blended together at room temperature and stirred until completely homogenous.

5 Dye 1

Dye (1)

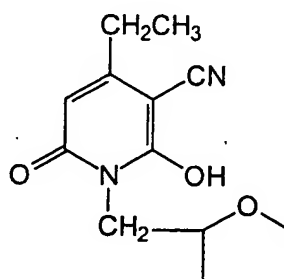
Dye (1) was prepared using stages 1a to 1c described below:

10

Stage 1a

4-nitrobenzoylchloride (55.7g) in CH_2Cl_2 (100ml) was added dropwise to a mixture of 2-(2-methoxyethoxy)ethanol (36g) and pyridine (32ml) in CH_2Cl_2 (200ml) keeping the temperature below 10°C . After isolation the resultant nitro compound was converted to the corresponding amino compound using H_2 gas and palladium catalyst in ethanol.

15

Stage 1b

20

Ethyl propionylacetate (72.14g) was added dropwise over 30 minutes to a stirred mixture of tetrahydrofurfurylamine (122.92g) and water (18g) at room temperature. Ethyl cyanoacetate (56.6g) was then added. After heating to 90°C for 20 hours the solution was cooled and poured onto ice (150g) and acidified by addition of concentrated hydrochloric acid. The product was filtered off, washed with water and dried at 45°C under reduced pressure to give 67.5g of the desired product.

Stage 1c

The product from Stage 1a (11.9g) was added to a mixture of water (30ml) and hydrochloric acid (12.3ml) and the solution cooled to 0-5°C. A solution of sodium nitrite (3.46g) in the minimum of water was then added dropwise keeping the temperature at 0-5°C. After stirring for a further 20 minutes the excess nitrous acid was destroyed by the addition of sulphamic acid. The resulting diazonium salt solution was slowly added to a solution of the product from stage 1b (12.4g) in methanol (200 ml) keeping the temperature < 10°C. After stirring for a further 30 minutes the yellow suspension was diluted with water (200 ml) and the product filtered-off and recrystallised from methanol to give 15.8g of the title product. $\lambda_{\text{max}} = 434 \text{ nm}$.

Dye 2

The method of Example 1 was repeated except that in place of ethyl propionylacetate there was used ethyl acetoacetate (65.07g).

The resultant Dye 2 had a λ_{max} at 434nm.

Dye 3

The method of WO98/14523, Example 1, stages 2a to 2e were followed to give the pyrazole dye shown on page 12, lines 15-20 of WO 98/14523. This dye is referred to as "Dye 3" in the following examples.

Dye 4

Dye 4 may be prepared by mixing together the dye described in WO98/59008, Example 1 (3 parts) and the dye described in WO98/59007, Example 1 (2 parts), or alternatively by co-synthesis of these dyes

Dye 5

Dye 5 was prepared by the method described in International patent application number PCT/GB/99/02453, Example 1.

Dye 6

Dye 6 was prepared by the method described in GB 2335924, Example 1.

Examples 1 to 6 and Comparative Examples 1 to 3

Inks were prepared having the compositions described in Table 1 below wherein all figures are in parts by weight. In each case the relevant dye was dissolved in benzyl alcohol and sonicated until the dye was in solution. Resin X (20% w/v in water) at pH 7.0 \pm 0.5 was then added, along with water and all additional components specified in Table 1.

Table 1

Dye	Ex 1	Ex 2	Ex 3	Ex 4	Ex 5	Ex 6	Comp Ex.1	Comp Ex.2	Comp Ex.3
Dye 1			3	3			3	3	3
Dye 2	2								
Dye 3		1.5			1.5	1.5			
Benzyl Alcohol	10	10	12	12	12	20	10	12	10
2-Pyrrolidone	20	20	20		20	20	20	20	20
Tetrahydrofurfuryl alcohol				20					
Nonyl Phenol + 6.5 EO [#]		4							
Tergitol 15-S-7 [*]	3								
Di-iso octyl sulphosuccinate			3	3	3	1		6	
Resin X (100% Solids)	2	4	4	4	4		9		4
Water	62	60.5	58	58	59.5	57.5	58	59	63

*A secondary alcohol ethoxylate obtained from Union Carbide

5 # a non-ionic surfactant free from carbon-carbon triple bonds

Ex = Example

Comp = Comparative Example

Printing Results

10 The described in Table 1 were used to fill empty colour cartridges from an Olivetti JP450 ink jet printer. This printer was then used to print the inks on Xerox 4024 plain paper from Rank Xerox. The optical density of the prints ("ROD") was measured and the print quality assessed visually.

The printing results are shown in Table 2 overleaf.

15

Example 7

Further inks may be prepared having the formulations described in Tables 3 and 4 below wherein the following abbreviations are used. These inks may be applied to a substrate such as plain paper using an ink jet printer.

TABLE 2

	Ex 1	Ex 2	Ex 3	Ex 4	Ex 5	Ex 6	Comp Ex 1	Comp Ex 2	Comp Ex 3
Ink Stability	>2wk	>1mth	>1mth	>1mth	>1mth	>2wk	>1mth	>1mth	<5min
Ink Viscosity ^[1]	-	-	4.7cps	-	5.0cps	5.0cps	8.5cps	-	N/A
Surface Tension	-	35.5	35.0	-	35.5	-	42.5	-	N/A
Print ROD	0.798	1.052	0.897	0.856	1.002	-	0.829	0.831	N/A
Print Light Fastness ^[2]	-	-	20.47	13.69	20.81	-	9.75	29.65	N/A
Print Quality	good	good	good	good	good	-	poor	good	N/A
Strike through	v.low	light	v.low	v.low	light	-	v.low	heavy	N/A

- = property not measured,

[1] = measured at 25°C using a Bohlin VOR rheometer

[2] = measured on Atlas Ci35 Weatherometer. The values quoted are the ΔE after 100 hours irradiation, with lower figures representing better light fastness than higher figures.

TABLE 3

Dye	Dye Content	Water	Resin (parts)	BZ	DEG	ACE	NaOH	SUR (parts)	IPA	MEOH	2P	MIBK	BUT
1	2.0	56	X(6)		6	4		A (2)			10	10	
2	3.0	59.8	X(8)	5	5		0.2	B (3)			15		
1	2.1	59.9	X(4)	8				C (1)			20	1	2
3	1.1	61.4	X(8)		9		0.5	D (0.5)			9	5	1
1+2	5	52	X(5)	15	3	3		C (2)	6		5	4	
3	5	45	X(10)	20				D (5)	10				
2	2.4	49.6	X(5)	4		5		B (2)		6	20	5	1
3	2	67.6	X(8)	5	2	10		A (1)					
1	3.2	55.8	X(4)	5	4	6		B (2)	5	4	6	5	
1	5	66	X(10)	6	2	2		C (4)	1		4		
3	1.8	59.2	X(2)	5				D (4)			15		5
1	3.3	62.7	X(8)			10		D (1)		2		6	3
2	2.0	60	X(5)	10		7	0.3	C (2.7)	3		10		
3	2.5	47.6	X(4)	20	2	1		D (2)			15	3	
1	1.0	62	X(7)	5	4			C (1)			15	5	

TABLE 4

Dye	Dye Content	Water	Resin (parts)	BZ	NMP	SUR (Parts)	TEN	TDG	FRU	PHO	DMB	CH ₃ NH ₂	CAP
3	1.5	60	X(4)	5		A (3)	0.5	20					
1	2.5	55	X(8)	6	15	B (2)				0.12			4
1	3.1	61	X(10)	8		C (3)		15				0.2	
3	0.9	58	X(2)	10	20	D (5)			0.5	0.2			
2	4.0	54	X(8)	10	4	C (2), B (1)			1		4	0.2	
3	2.2	63	X(6)	10	3	C (4.1)			2		6		
3	5.0	53	X(8)	11		C (4)		10			6		1
1	5.4	53	X(10)	5	17	B (1)					7		
3	2.1	61	X(5)	5	5	C (4)	0.2	2	0.5	0.1	5		
2	2	55	X(4)	10	5	B (1)		12			5		
3	2.0	41	X(8)	5	8	D (3)					5		12
1	4	46	X(7)	15	2	C (4)					12		
1	1.0	78	X(5)	10		A (2)	1	1				1	1

FRU : fructose

Resin : The number of parts by weight of resin is shown in brackets. The resins are preferably added as 20% w/w solution/dispersion in water.

BZ : Benzyl alcohol

5 DEG : Diethylene glycol

DMB : Diethyleneglycol monobutyl ether

ACE : Acetone

IPA : Isopropyl alcohol

MEOH : Methanol

10 2P : 2-Pyrrolidone

MIBK : Methylisobutyl ketone

SUR : Surfactant A is sodium dodecyl benzene sulphonate; surfactant B is Nonyl phenol + 6.5 EO; surfactant C is diisooctyl sulphosuccinate of the formula $\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{OCOCH}(\text{SO}_3\text{H})\text{CH}_2\text{COOCH}_2\text{CH}(\text{C}_2\text{H}_5)(\text{CH}_2)_3\text{CH}_3$; surfactant D is

15 Tergitol 15-S-7(a secondary alcohol ethoxylate)

PHO : K_2PO_4

TEN : triethanolamine

NMP : N-methyl pyrrolidone

TDG : Thiodiglycol

20 CAP : Caprolactam

BUT : Butylcellosolve

Examples 8 to 18 and Comparative Example 4

25 The inks shown in Table 5 below were prepared by the general method described in Examples 1 to 6 above.

Printing Results

30 The inks described in Table 5 were used to fill empty colour cartridges from an Olivetti JP192 ink jet printer. This printer was then used to print the inks on to the following substrates:

Xerox™ 4024 - a plain paper from Rank Xerox

Canon™ HG201 - a glossy ink jet film supplied by Canon

Epson™ Glossy Ink Jet Film - supplied by Epson

35 The optical density (ROD), chroma (brightness) and light-fastness of the prints were measured.

In the evaluation of light-fastness the prints were faded in an Atlas Ci35 Weatherometer for 100 hours. The degree of fade is expressed both as the % loss in ROD and also ΔE .

Table 5													
	Ex. 8	Ex. 9	Ex. 10	Ex. 11	Ex. 12	Ex. 13	Ex. 14	Ex. 15	Ex. 16	Ex. 17	Ex. 18	Comp Ex 4	
Dye 4	3	3	3	3.00	3	3	3	3	3	3	3	3	
Benzyl Alcohol	12	12	12	12.00	12	12	12	12	12	12	12	12	
2-Pyrrolidone	20	20	20	20.00	20	20	20	20	20	20	20	20	
Di-isooctyl sulphosuccinate	3						1.5						
Solsperse 27000		3					1.5						
Sodium Lauryl Sulphate			3	1.50									
Synperonic PE L72				1.50									
Empimin MH					3								
Empimin MKB						3							
Tween 80								3	6				
Synperonic PE L35										3			
Synperonic PE P85											3		
Surfynol 465												3	
Resin X (100% solids)	4	4	4	4.00	4	4	4	4	4	4	4	4	
Water	58	58	58	58.00	58	58	58	58	55	58	58	58	

ΔE is defined as the overall change in the CIE colour co-ordinates L^* , a^* , b^* of the print and is expressed by the equation $\Delta E = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{0.5}$. A high figure for ΔE indicates low light-fastness.

- 5 The results are shown below in Tables 6, 7 and 8.

Table 6 - Xerox 4024

	Chroma	Initial ROD	Light Fastness Data		
Example			ROD after fading	% OD loss	ΔE
8	81.09	0.765	0.449	41.31	32.71
9	72.15	0.669	0.283	57.70	43.91
10	82.67	0.8	0.469	41.38	31.31
11	81.85	0.782	0.427	45.40	35.47
12	65.15	0.607	0.41	32.45	13.57
13	78.11	0.742	0.559	24.66	15.57
14	86.47	0.858	0.535	37.65	27.49
15	77.87	0.731	0.391	46.51	35.75
16	67.43	0.619	0.245	60.42	40.83
17	80.03	0.755	0.397	47.42	35.17
18	83.89	0.803	0.427	46.82	34.29
Comp Ex 4	63.35	0.568	0.162	71.48	47.48

Table 7 - Canon HG201

	Chroma	Initial ROD	Light Fastness Data		
Example			ROD after fading	% OD loss	ΔE
8	101.47	0.917	0.213	76.77	78.85
9	112.91	1.069	0.213	80.07	87.01
10	104.73	0.968	0.294	69.63	73.07
11	105.89	0.984	0.258	73.78	75.05
12	114.65	1.116	0.343	69.27	70.45
13	109.35	1.03	0.358	65.24	62.67
14	113.47	1.114	0.312	71.99	75.83
15	105.53	0.966	0.168	82.61	89.25
16	94.69	0.823	0.085	89.67	93.47
17	110.75	1.046	0.261	75.05	78.19
18	109.19	1.004	0.159	84.16	91.75
Comp Ex 4	80.99	0.677	0.07	89.66	90.53

Table 8 - Epson Glossy Film

Example	Chroma	Initial ROD	Light Fastness Data		
			ROD after fading	% OD loss	ΔE
8	92.61	0.822	0.21	74.45	72.23
9	100.53	0.96	0.21	78.13	73.09
10	99.67	0.933	0.321	65.59	58.29
11	103.23	0.976	0.344	64.75	60.35
12	110.81	1.088	0.306	71.88	66.29
13	110.27	1.067	0.426	60.07	50.55
14	106.09	1.039	0.318	69.39	65.81
15	100.99	0.918	0.257	72.00	64.91
16	87.01	0.753	0.156	79.28	72.47
17	106.23	1.006	0.287	71.47	67.01
18	102.65	0.958	0.31	67.64	62.05
Comp Ex 4	83.35	0.713	0.124	82.61	70.89

Examples 19 to 28

The inks shown in Table 9 below were prepared by the general method described in Examples 1 to 6 above.

Printing Results

The inks described in Table 9 were used to fill empty colour cartridges from an Olivetti JP192 ink jet printer. This printer was then used to print the inks onto substrates precisely as described above in relation to Examples 8 to 18:

- 5 The results of tests performed on the substrates are shown in Tables 10, 11 and 12 below (ROD, chroma, % OD loss, ΔE and media are as described above in relation to Examples 8 to 18)

Table 10 - Xerox 4024

	Chroma	Initial ROD	Light Fastness Data		
Example			ROD after fading	% OD loss	ΔE
19	38.03	0.786	0.67	14.76	8.33
20	32.99	0.697	0.62	11.05	6.69
21	36.09	0.745	0.677	9.13	5.17
22	37.61	0.785	0.661	15.80	8.59
23	36.15	0.741	0.622	16.06	9.53
24	36.37	0.765	0.701	8.37	5.35
25	36.29	0.759	0.68	10.41	6.29
26	37.69	0.807	0.674	16.48	8.21
27	35.21	0.73	0.606	16.99	9.25
28	35.37	0.728	0.635	12.77	7.21

Table 11 - Canon HG201

	Chroma	Initial ROD	Light Fastness Data		
Example			ROD after fading	% OD loss	ΔE
19	45.21	0.949	0.873	8.01	4.59
20	47.09	1.008	0.971	3.67	5.81
21	43.61	0.898	0.841	6.35	5.39
22	44.13	0.91	0.828	9.01	5.23
23	52.95	1.362	1.264	7.20	6.03
24	52.39	1.32	1.089	17.50	5.79
25	47.99	1.063	0.99	6.87	5.01
26	51.49	1.253	1.112	11.25	4.95
27	48.99	1.097	0.965	12.03	5.39
28	44.37	0.907	0.836	7.83	6.07

Table 12 - Epson Glossy Film

Example	Chroma	Initial ROD	Light Fastness		
			Data ROD after fading	% OD loss	ΔE
19	44.41	0.973	0.767	21.17	8.25
20	43.33	1.055	0.876	16.97	8.21
21	43.19	0.918	0.832	9.37	4.73
22	41.91	0.871	0.61	29.97	11.69
23	50.45	1.268	1.106	12.78	5.47
24	47.17	1.066	0.989	7.22	4.63
25	46.41	1.039	0.863	16.94	7.23
26	49.79	1.224	1.055	13.81	5.75
27	47.33	1.072	0.908	15.30	6.59
28	44.13	0.937	0.747	20.28	8.71

Examples 29 to 34 and Comparative Examples 5 to 8

5 The inks shown in Table 13 below were prepared by the general method described in Examples 1 to 6 above.

Table 13

	Ex. 29	Comp.Ex.5	Ex. 30	Ex. 31	Ex. 32	Comp.Ex.6	Ex. 33	Comp.Ex.7	Ex. 34	Comp.Ex. 8
Dye 4							3	3	3	3
Dye 5	3	3		3	3	3				
Dye 6			3							
Benzyl Alcohol	12	12	12	12	12	12	12	12	12	12
2-Pyrrolidone	20	20	20	20	20	20	20	20	20	20
Solsperse 27000	3							3		
Sodium Lauryl Sulphate			1.5	1						
Synperonic PE L72			1.5							
Empimin MH				3			3			
Surfynol 465		3						3		3
Resin V (as 100% solids)				4	4	9				
Resin W (as 100% solids)	4	4							4	4
Resin Y (as 100% solids)			4							
Resin Z (as 100% solids)				4			4	4		
Water	58	58	58	58	60	56	58	58	58	58

Printing Results

The inks described in Table 13 were used to fill empty colour cartridges from an Olivetti JP192 ink jet printer. This printer was then used to print the inks on to a range of substrates as shown below in Table 14.

- 5 The optical density (ROD), chroma (brightness) and light fastness of the prints were measured as described above in relation to Examples 19 to 28.

Table 14				Light Fastness - 100 hrs exposure		
	Print Media	Chroma	Initial ROD	ROD	% OD loss	ΔE
Example 29	XA	33.93	0.737	0.621	15.74	7.61
Example 29	HG 201	44.21	0.919	0.785	14.58	5.91
Example 29	Ep.Gl.Film	46.35	1.059	0.851	19.64	8.01
Comp.Ex.5	Ep.Gl.Film	44.59	0.952	0.693	27.21	8.21
Example 30	XA	54.01	0.975	0.623	36.10	18.15
Example 31	XA	32.17	0.652	0.573	12.12	6.83
Example 31	Ep.Gl.Film	44.75	1.013	0.747	26.26	8.61
Example 31	HG 201	44.77	0.957	0.906	5.33	4.69
Example 32	Ep.Gl.Film	44.35	0.983	0.724	26.35	10.29
Example 32	HG 201	44.29	0.937	0.773	17.50	5.11
Example 32	XA	35.79	0.719	0.588	18.22	7.67
Comp.Ex.6	too viscous - would not print					
Example 33	Ep.Gl.Film	85.01	0.784			
Example 33	HG 201	85.91	0.776			
Example 33	XA	78.59	0.77			
Comp.Ex.7	No print - dye crashed out of solution / some deposit					
Example 34	Ep.Gl.Film	104.37	1.023			
Comp. Ex.8	Ep.Gl.Film	101.55	0.978			

XA = Xerox Acid Paper

- 10 HG 201 = Canon HG 201 - a glossy ink jet film from Canon

Ep.Gl.Film = Epson glossy ink jet film

CLAIMS

1. A composition comprising a water-dissipatable polymer, dye, surfactant, water and organic solvent, wherein the surfactant comprises :
 - 5 (a) a surfactant having a sulpho or sulphate group; or
 - (b) a non-ionic surfactant free from carbon-carbon triple bonds; or
 - (c) a mixture of (a) and (b).
2. A composition according to claim 1 comprising
 - 10 (i) from 30 to 95 parts of water;
 - (ii) from 1 to 70 parts of organic solvent;
 - (iii) from 0.1 to 20 parts of dye;
 - (iv) from 0.25 to 40 parts of water-dissipatable polymer;
 - 15 (v) from 0.1 to 15 parts of said surfactant.
3. A composition according to any one of the preceding claims wherein the water dissipatable polymer is a water-dissipatable acrylic, polyurethane or polyester polymer.
4. A composition according to any one of the preceding claims wherein the water-
20 dissipatable polymer bears non-ionic and/or ionic water-dispersing groups.
5. A composition according to any one of the preceding claims wherein the dye is a disperse or solvent soluble dye.
- 25 6. A composition according to any one of the preceding claims wherein the dye is a disperse or solvent soluble dye carrying a branched alkylamino group.
7. A composition according to any one of the preceding claims wherein the surfactant comprises an alkyl benzene sulphonic acid salt, an aromatic sulphonic acid salt, a mono-
30 or di- alkyl sulphosuccinic acid salt, a mono- or di- alkyl sulpho succinamate or a mono- or di-alkyl ethoxy sulphosuccinate.
8. A composition according to any one of the preceding claims wherein the surfactant comprises a mono- or di- alkyl sulphosuccinate or a mono- or di-alkyl sulphosuccinamate.
35
9. A composition according to any one of the preceding claims wherein the surfactant comprises a di-isooctyl sulphosuccinate.
10. A composition according to any one of the preceding claims wherein the organic
40 solvent comprises a water-miscible solvent and a water-immiscible solvent.

11. A composition according to claim 10 wherein the water-immiscible solvent comprises benzyl alcohol.
- 5 12. An ink composition according to any one of the preceding claims suitable for use in thermal and/or piezoelectric ink jet printers.
- 10 13. A process for printing an image on a substrate comprising applying thereto a composition or ink according to any one of the preceding claims by means of an ink jet printer.
14. A process according to claim 13 wherein the substrate is a paper, an overhead projector slide or a textile material.
- 15 15. A paper, an overhead projector slide or a textile material printed with a composition according to any one of claims 1 to 12.
16. An ink jet printer cartridge containing a composition according to any one of claims 1 to 12.

INTERNATIONAL SEARCH REPORT

Intern. Appl. No.

PCT/GB 99/04061

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09D11/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	US 5 883 157 A (YAMASHITA YOSHIRO ET AL) 16 March 1999 (1999-03-16) column 2, line 48 -column 3, line 5 column 3, line 53 -column 4, line 11 column 4, line 36-39 column 5, line 55 -column 6, line 15 column 6, line 44-60	1-3, 7, 12-16
X	-& JP 09 157564 A (FUKI XEROX) 17 June 1997 (1997-06-17)	
X	US 5 441 561 A (CHUJO AKIHIKO ET AL) 15 August 1995 (1995-08-15) column 1, line 24, 25 column 2, line 39-64 column 3, line 65 -column 4, line 33 column 4, line 34-60 column 4, line 61-64	1, 3, 7, 12-16

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. Appl. No.

PCT/GB 99/04061

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			JP	7082515 A	28-03-1995

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